

**DOT/FAA/AR-01/32**

Office of Aviation Research  
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# **Thermal Decomposition of Cyanate Ester Resins**

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Final Report

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1. Report No. DOT/FAA/AR-01/32		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle THERMAL DECOMPOSITION OF CYANATE ESTER RESINS				5. Report Date September 2001	
				6. Performing Organization Code	
7. Author(s) Michael L. Ramirez <sup>1</sup> , Richard Walters <sup>2</sup> , Edward P. Savitski <sup>3</sup> , and Richard E. Lyon <sup>4</sup>				8. Performing Organization Report No.	
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				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration Office of Aviation Research Washington, DC 20591				13. Type of Report and Period Covered Final Report	
				14. Sponsoring Agency Code AIR-100	
15. Supplementary Notes					
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17. Key Words Polymer, Polycyanurate, Cyanate ester, Thermoset polymer, Thermal degradation, Fire, Flammability			18. Distribution Statement This document is available to the public through the National Technical Information Service (NTIS), Springfield, Virginia 22161.		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 20	
				22. Price	

## ACKNOWLEDGEMENTS

The authors are grateful to Dave Shimp for many helpful discussions and to David Esral for determining the char-forming tendency of some of the polycyanurates. Certain commercial equipment, instruments, materials, or companies are identified in this report in order to adequately specify the experimental procedure. This in no way implies endorsement or recommendation by the Federal Aviation Administration.

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## EXECUTIVE SUMMARY

Polycyanurate networks were prepared by thermal polymerization of cyanate ester monomers containing two or more cyanate ester ( $-O-C\equiv N$ ) functional groups. The thermal decomposition chemistry of nine different polycyanurates was studied by thermogravimetry, infrared analysis of solid films, and analysis of the gases evolved during pyrolysis using infrared spectroscopy and gas chromatography-mass spectrometry. It was found that the thermal stability of the polycyanurates was essentially independent of monomer chemical structure with the major mass loss occurring at about 450°C for all materials. Analysis of the solid-state and gas phase thermal degradation chemistry indicates a thermal decomposition mechanism for polycyanurates which begins with hydrocarbon chain scission and cross-linking at temperatures between 400°-450°C with negligible mass loss, followed by decyclization of the triazine ring at 450°C that liberates volatile cyanate-ester decomposition products. The solid residue after pyrolysis increases with the aromatic content of the polymer and incorporates about two thirds of the nitrogen and oxygen present in the original material.

## 1. INTRODUCTION.

Polycyanurates are addition-cured thermoset polymers that exhibit good [1-4] to outstanding [5 and 6] fire resistance. Because the ignition and fire resistance of solid polymers are governed by short term thermal stability and anaerobic degradation chemistry [7-10], the following study was conducted to understand these processes in polycyanurates. Polycyanurates are formed when three cyanate ester monomers containing the  $-O-C\equiv N$  functional group undergo a thermally initiated cyclotrimerization (addition) reaction [11 and 12] to form a six-member oxygen-linked triazine ring (cyanurate) as illustrated in figure 1.

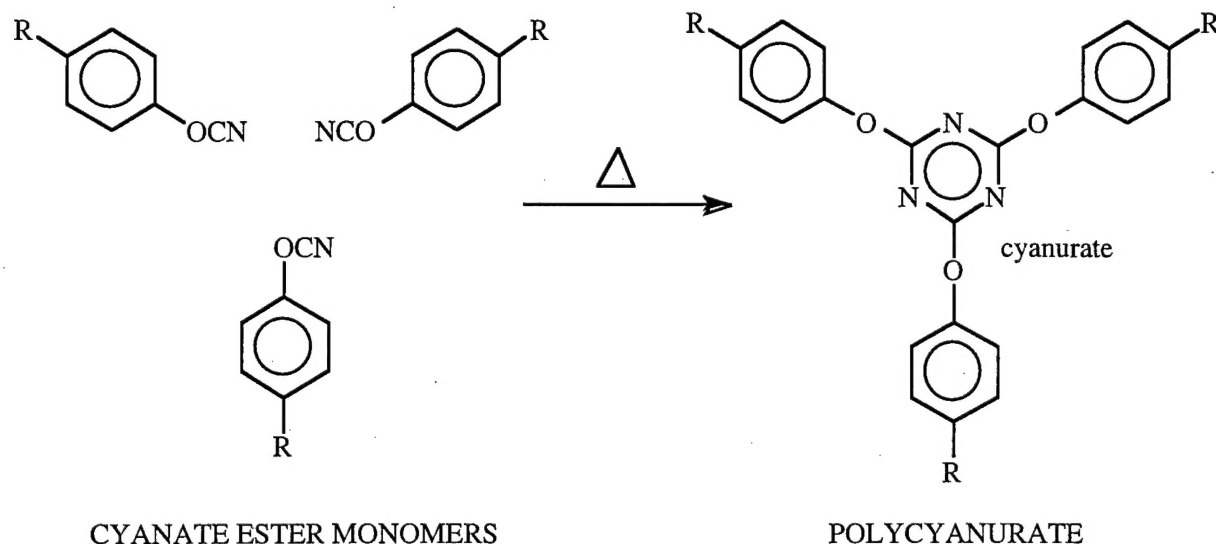


FIGURE 1. CYANATE ESTER POLYMERIZATION REACTION

The cyanurate is a thermally stable cross-link that is responsible for the high mass loss temperature ( $450^{\circ}\text{C}$ ) of these thermosets. Polycyanurates derived from phenol novolac cyanate esters have a high glass transition temperature  $T_g > 350^{\circ}\text{C}$  approaching their thermal decomposition temperature [13 and 14]. In addition to having high thermal stability, polycyanurates form a carbonaceous char during burning that protects the underlying material and further enhances fire resistance [15 and 16]. Because cyanate ester resins polymerize by an addition reaction, no volatiles or by-products are produced during cure which can cause voids and subsequent loss of strength in the final product [14-16]. Thermogravimetric studies of polycyanurates in air have indicated that thermoxidative degradation proceeds via rapid hydrolysis of the ether oxygen bond between the phenyl and triazine rings in the presence of moisture at temperatures of  $350^{\circ}\text{C}$ - $420^{\circ}\text{C}$  [17-19]. Purely thermal degradation under anaerobic conditions is claimed at higher temperature ( $\geq 450^{\circ}\text{C}$ ) via homolytic cleavage of the hydrocarbon backbone over a narrow temperature range ( $450^{\circ}\text{C}$ - $500^{\circ}\text{C}$ ) independent of the chemical structure of the linking groups between the cyanurate rings [18-20]. The present study extends these previous thermogravimetric studies of polycyanurate thermal degradation to include infrared and mass spectroscopic analysis of the solid and gaseous pyrolysis products.



## 2. EXPERIMENTAL.

### 2.1 MATERIALS.

Nine cyanate ester monomers (resins) with different chemical structures were examined in this study. The monomer structures and suppliers are shown in table 1. Five of the resins are difunctional cyanate esters derived from bisphenols, while two of the resins are multifunctional resins derived from phenol novolacs. All of the cyanate ester resins were used as received from the manufacturer without modification, purification, or catalysts. With the exception of the bisphenol C (BPC) cyanate ester, which is a research monomer at present, all of the resins examined in this study are commercial materials. The BPC polycyanurate was included in this study because of its unusually high fire resistance [5 and 6] and because the dichloro-diphenyl-ethylene unit linking the cyanurate rings is quantitatively converted to char and hydrogen chloride during pyrolysis [20], isolating the role of the cyanurate ring in thermal degradation. Solid polycyanurate samples were obtained from cyanate ester monomers (see figure 1) by polymerization in a forced air convection oven at 100°C for 30 minutes, 150°C for 30 minutes, 200°C for 60 minutes, and 250°C for 3 hours as per the manufacturer's recommended temperature program [14]. Phenol novolac cyanate esters were postcured at 300°C for an additional 30 minutes. All gases used for experiments were ultra-high-purity (>99.999%) grades obtained from Matheson Gas Products.

### 2.2 THERMAL ANALYSES.

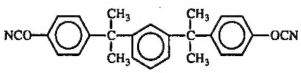
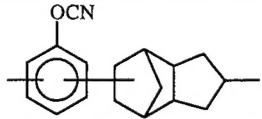
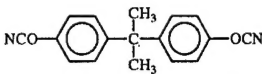
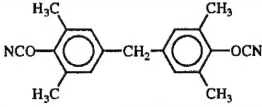
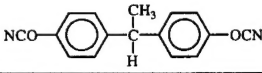
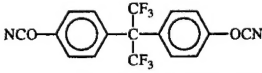
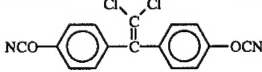
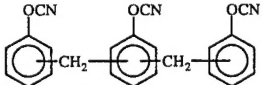
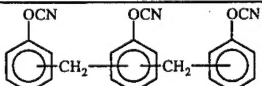
A thermogravimetric analyzer (Perkin Elmer TGA 7) was used to study the anaerobic mass loss processes accompanying thermal degradation of cured samples. The TGA cell was purged for 20 minutes with flowing nitrogen (100 cm<sup>3</sup>/min), after which the sample was heated from 200° to 900°C at a constant rate of 10°C/minute.

### 2.3 INFRARED SPECTROSCOPY.

#### 2.3.1 Solid Films.

A temperature-programmable cell (The Hot-One, CIC Photonics) positioned in the beam of a Fourier transform infrared (FTIR) spectrometer (Magna 550 FTIR, Nicolet Instruments) was used to collect infrared spectra of thin films cast from acetone solution during or after polymerization. Samples were heated between 25° and 675°C in a nitrogen purge at a constant heating rate of 10°C/min. The temperature of the film was monitored using a thermocouple in contact with the sample. The FTIR spectra of the films were obtained using 32 scans at a resolution of 4 cm<sup>-1</sup>.

TABLE 1. CYANATE ESTER MONOMERS

Monomer Structure	Material/CAS Registry Number	Trade Name	Supplier	Molecular Weight (g/mole)
	Bisphenol M Cyanate Ester [127667-44-1]	Arocy XU-366	Ciba	396.49
	Dicyclopentadienylbisphenol Cyanate Ester [135507-71-0]	Arocy XU-71787	Dow	251.32
	Bisphenol A Cyanate Ester [1156-51-0]	Arocy B-10	Ciba	278.31
	Tetramethylbisphenol F Cyanate Ester [101657-77-6]	Arocy M-10	Ciba	306.36
	Bisphenol E Cyanate Ester [47073-92-7]	Arocy L-10	Ciba	264.28
	Hexafluorobisphenol A Cyanate Ester [32728-27-1]	Arocy F-10	Ciba	386.25
	Bisphenol C Cyanate Ester [not assigned]	RD98-228	Ciba	331.16
	Phenol Novolac Cyanate Ester [30944-92-4]	Arocy XU-371	Ciba	381.39
	Phenol Novolac Cyanate Ester [173452-35-2]	Primaset PT-30	Lonza	381.39

### 2.3.2 Pyrolysis Gases.

A commercial probe pyrolyzer (Pyroprobe 2000, CDS Analytical), heated gas cell (Pyroscan/IR, CDS Analytical), and FTIR spectrometer (Magna 550 FTIR, Nicolet Instruments) were used to obtain gas phase infrared spectra of the volatile polycyanurate decomposition products. The pyrolysis probe-gas cell arrangement allows solid samples to be thermally decomposed directly in the FTIR beam so that infrared spectra of the gaseous decomposition products are obtained instantaneously. In the experiments, approximately 15 mg of sample in a quartz tube (3 mm outside diameter by 12 mm long) was placed in the heating coil of the probe pyrolyzer which was then inserted into a heated gas cell with a working volume of 20 cm<sup>3</sup>. The gas cell was maintained at 200°C and purged with nitrogen at a flow rate of 20 cm<sup>3</sup>/min for 20 minutes prior to, and continuously during, the experiment in which samples were heated from 200° to 1000°C

at a constant heating rate of 20°C/min. One spectrum (16 scans, 4-cm<sup>-1</sup> resolution, gain 1.0) was collected each minute of the heating program in synchronization with the cell turnover time.

## 2.4 PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROMETRY.

A commercial pyrolysis probe (Pyroprobe 2000, CDS Analytical) interfaced to a coupled gas chromatograph (GC) mass spectrometer (MS) with an electron impact detector (Hewlett Packard 5890) was used for identification of the pyrolysis products of thermal decomposition. A sample of about 30-100 µg of the cured polycyanurate was placed in a quartz tube (3 mm outside diameter by 12 mm in length) and the ends plugged with glass wool. The sample was then loaded into the pyrolysis probe and placed into a heated interface. The interface and GC/MS inlet were maintained at 275°C and purged with helium and samples were heated from 275° to 750°C at 10°C/min. The pyrolysis products were adsorbed onto the 40°C capillary column of the gas chromatograph (HP-5 cross-linked silicone column measuring 0.32 mm by 25 m with a 0.52-µm film thickness) and then desorbed into the mass spectrometer at a heating rate of 10°C/min to a final temperature of 295°C. The mass range used for the mass selective detector was 36 to 400 mass/charge ratio (m/z). The mass spectra of the decomposition products were identified using mass spectral libraries (Wiley, NBS75k, and UMass) at a qualification percentage of 80% or higher.

## 3. RESULTS AND DISCUSSION.

### 3.1 POLYMERIZATION CHEMISTRY.

Figure 1 showed the chemistry of the cyanate ester polymerization to polycyanurate. The characteristic absorption bands of the -O-C≡N cyanate ester functional group are observed in the infrared spectrum between 2200-2300 cm<sup>-1</sup> [12 and 21]. The band is usually split into a doublet or triplet of partially resolved peaks depending on the chemical environment of the cyanate ester. When the absorption appears as a doublet, the peaks are typically separated by approximately 38 cm<sup>-1</sup>. The polymerization (curing) of cyanate ester resins can be followed by monitoring the disappearance of the cyanate ester absorbance bands and/or the corresponding increase in the absorbance bands of the triazine ring near 1360 and 1570 cm<sup>-1</sup> [12 and 22] as illustrated in figure 2 for the polymerization of a solvent-cast film of B-10.

The cyclotrimerization reaction occurs between 100° and 200°C for this heating program, (20°C/min) as indicated by the disappearance of the cyanate ester bands at 2200-2300 cm<sup>-1</sup>, and the appearance of 1370- and 1565-cm<sup>-1</sup> triazine peaks. The polymerization can go to completion (100% reaction of cyanate ester groups) only at temperatures above the glass transition (vitrification) temperature of the polycyanurate, which for these materials ranges from 192°C for XU-366 to >350°C for PT-30 and XU-371 (see table 2).

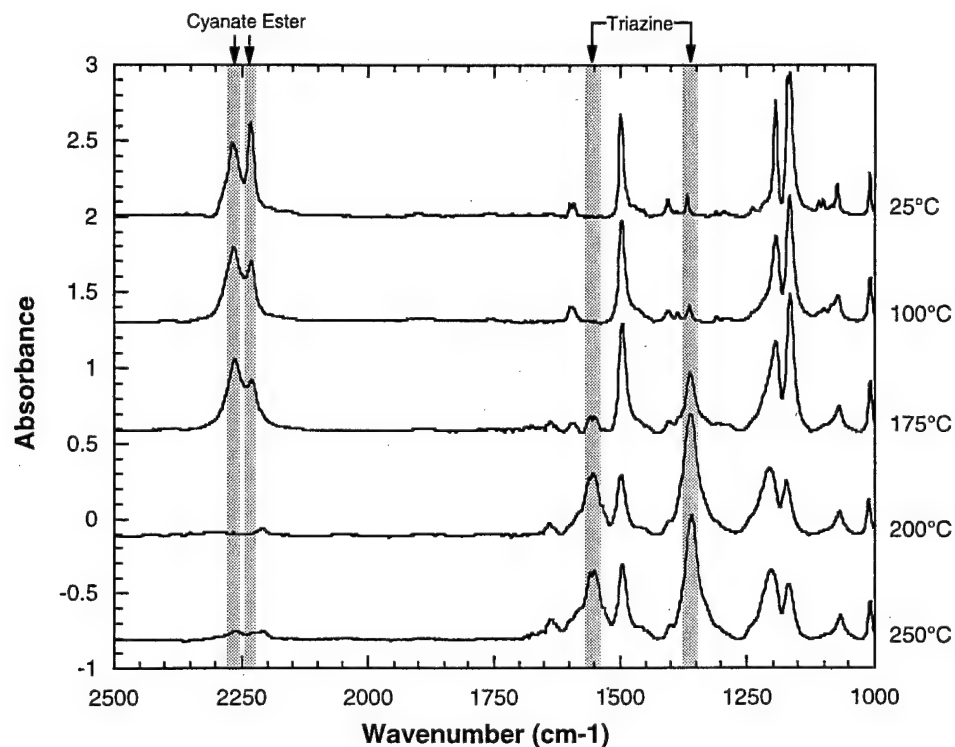


FIGURE 2. FOURIER TRANSFORM INFRARED CURE MONITORING OF B-10 CYANATE ESTER RESIN

TABLE 2. THERMAL PROPERTIES OF POLYCYANURATES

Sample	Glass Transition Temperature (°C)	5% Weight Loss Temperature (°C)	Peak Mass Loss Rate Temperature (°C)	Char Yield at 900°C (%)
XU-366	192	439	482	31
XU-71787	244	447	463	33
B-10	257	443	468	39
M-10	252	443	471	41
L-10	258	455	479	47
F-10	270	453	465	49
BPCCE	275	441	461	56
XU-371	> 350	454	461	62
PT-30	> 350	457	462	63
Average:		448 ±7	468 ±8	

### 3.2 SOLID-STATE DEGRADATION CHEMISTRY.

Figure 3 shows TGA data for the nine samples between 300° and 900°C. Figure 4 shows the mass loss rate (derivative of the TGA) data for the PT-30 polycyanurate and the deconvolution of that data using an asymmetric double sigmoidal peak fit to isolate the individual mass loss processes that occur during heating. The data reveals that the polycyanurates thermally decompose in two steps with the major mass loss event beginning at about 450°C as reported in references 12, 17-19.

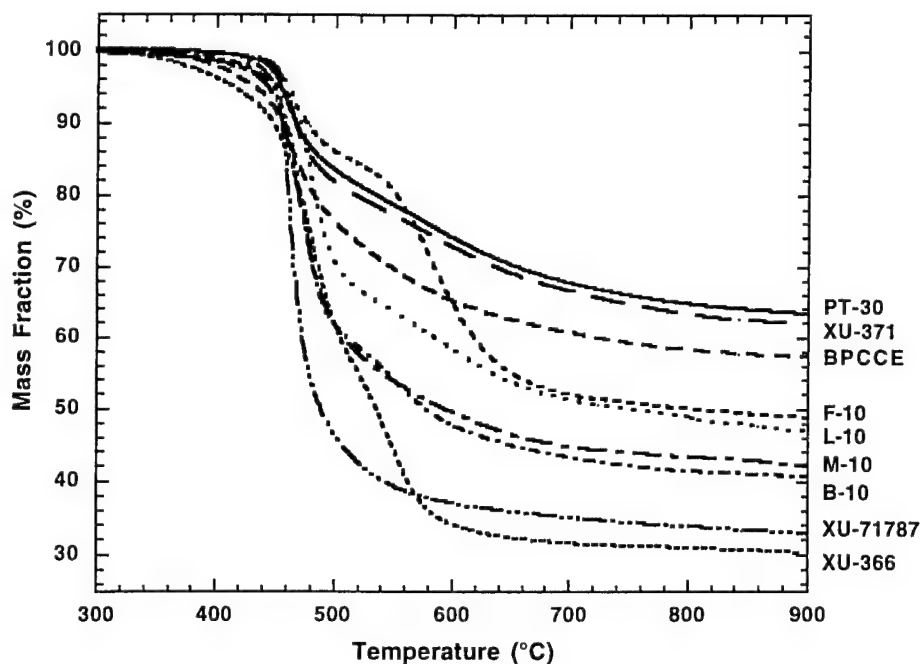


FIGURE 3. THERMOGRAVIMETIC DATA FOR THE NINE POLYCYANURATES

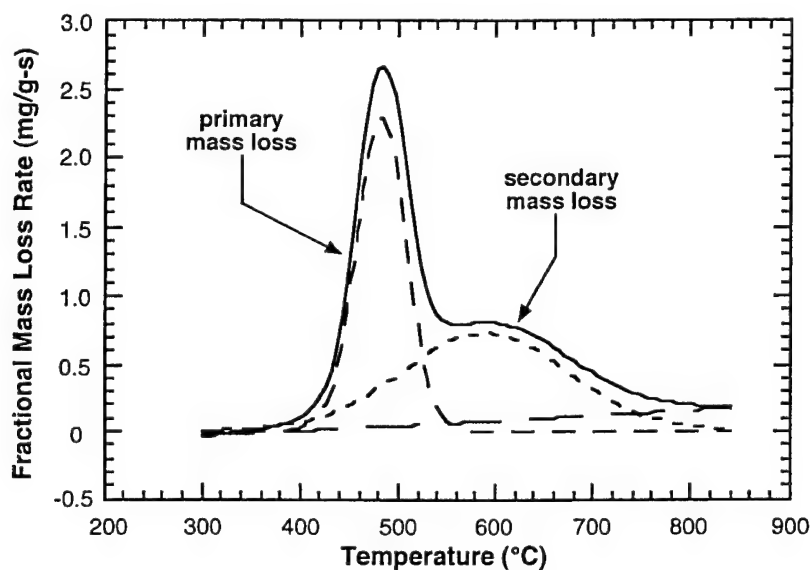


FIGURE 4. MASS LOSS RATE VERSUS TEMPERATURE FOR PT-30

Table 2 shows the temperature at 5% weight loss, the temperature at maximum mass loss rate, the char yield at 900°C, and the reported [12, 5, and 6] glass transition temperatures. Note that the 5% weight loss temperatures ( $448^{\circ} \pm 7^{\circ}\text{C}$ ) and the peak mass loss rate temperatures ( $468^{\circ} \pm 8^{\circ}\text{C}$ ) are relatively insensitive to monomer chemical structure for the nine polycyanurates tested. Conversely, the char yield is sensitive to the chemical structure of the monomer and increases with glass transition temperature and in rough proportion to the mole fraction of unsaturated carbon-carbon bonds.

The char yield of polymers has been empirically related to the char-forming tendency ( $C_{FT}$ ) of the individual chemical groups comprising the polymer repeat unit by Van Krevelen [7 and 8] who conducted anaerobic pyrolysis experiments on over 100 polymers [8]. In particular, the char-forming tendency is an additive molar quantity that is defined as the amount of char per structural unit divided by 12 (the atomic weight of carbon), i.e., the amount of carbon equivalents in the char per structural unit. The char-forming tendency of the cyanurate can be calculated by Van Krevelen's method using the reported char-forming tendencies of the chemical groups comprising the backbone of the cyanate ester monomers and the char yields of the polycyanurates reported in table 2. The individual results for the char-forming tendency of the cyanurate  $(OCN)_3$  calculated from the TGA data are B-10,  $C_{FT} = 6$  carbon equivalents per structural unit; L-10,  $C_{FT} = 7$  c-eq./unit; XU-366,  $C_{FT} = 8$  c-eq./unit; M-10,  $C_{FT} = 8$  c-eq./unit; and PT-30,  $C_{FT} = 9$  c-eq./unit. The average value of the char-forming tendency from these separate determinations is  $C_{FT} = 8 \pm 1$  carbon equivalents per cyanurate, meaning that on average, eight carbon-equivalent atoms are incorporated into the char for each three-carbon cyanurate.

Consequently, most of the nitrogen and oxygen in the cyanurate ring are also incorporated into the char, but at an efficiency that is 2-3 times higher than fused-aromatic heterocycles such as benzimides, benzimidazoles, and phenylquinoxalines [7 and 8]. Alternatively, the cyanurate could be interacting with other structural groups to increase their char-forming tendency during the process of thermal degradation—in which case the assumption of molar group additivity (noninteracting groups) is invalid.

The incorporation of oxygen and nitrogen into the char as deduced from molar group calculations is supported by elemental analyses of the polycyanurates chars recovered after flaming combustion in a fire calorimeter. Fire chars are formed under similar conditions as nitrogen-purged TGA chars, because in flaming combustion, the char reaches several hundred degrees centigrade and the thermal degradation process in the pyrolysis layer is anaerobic because atmospheric oxygen is consumed by the flame [9 and 10]. Consequently, fire and TGA chars should (and do) have comparable mass fraction [9 and 10] and composition. Elemental analysis of the virgin PT-30 polycyanurate gives  $C_{23}H_{15}O_3N_3$  for the repeat unit composition ( $C_{23}H_{15}O_3N_3$  theoretical) versus  $C_{23}H_7O_{2.7}N_{1.4}$  for the fire char. Similarly, the virgin BPC polycyanurate has measured (and theoretical) atomic composition  $C_{16}H_8O_2N_2Cl_2$  versus  $C_{16}H_3O_{1.3}N_{1.3}$  for the char. Chlorine is absent from the BPC polycyanurate fire char because all of the chlorine is evolved as hydrogen chloride during thermal degradation (see section 3.3). In summary, analysis of the chars from pyrolysis and burning shows that about 2/3 of the original oxygen and nitrogen in the polycyanurate remains in the char after anaerobic thermal degradation, with 1/3 leaving in volatile species.

Figure 5 contains a series of solid film infrared spectra of B-10 polycyanurate during heating at  $10^\circ\text{C}/\text{min}$  to  $675^\circ\text{C}$  under nitrogen. The infrared spectra of all of the polycyanurate films during thermal degradation are similar. There are no major changes in the solid film infrared spectra of the polycyanurates at temperatures below  $400^\circ\text{C}$ , indicating that very little thermal degradation has occurred. Above  $400^\circ\text{C}$ , the  $1570\text{-cm}^{-1}$  triazine band of the cyanurate ring decreases rapidly, while a  $2280\text{-cm}^{-1}$  absorbance band, tentatively assigned to isocyanate in the solid and/or carbon dioxide gas in the cell, increases in intensity over the same temperature interval, reaching a

maximum at 475°C. This pattern suggests thermal isomerization of the cyanurate to isocyanate [23]. Above 475°C, the 2280-cm<sup>-1</sup> band decreases again probably because of the elimination of hydrocyanic acid (HOCN) which is detected in the pyrolysis-GC/MS data. A common model for the degradation of the cyanurate involves the production of the volatile compounds CO, CO<sub>2</sub>, HCN, and ammonia [12, 17, 24, and 25]. In the present study, it appears that the first step in the solid degradation process involves isomerization of cyanurate to isocyanate which subsequently reacts with moisture to form carbamates that can further hydrolyze to carbamic acid, an unstable intermediate that spontaneously decomposes to CO<sub>2</sub> and ammonia [23]. Above 440°C weight loss begins in earnest and all of the infrared absorption bands for the solid decrease in intensity uniformly until only the optically black [26] char remains.

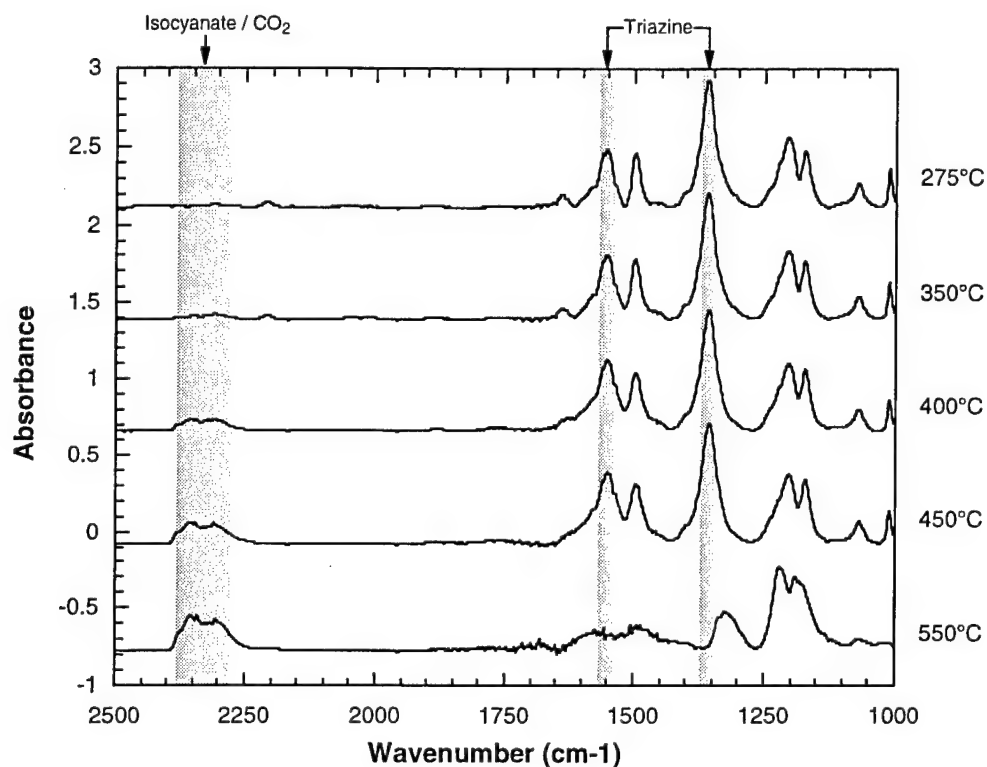


FIGURE 5. TEMPERATURE RESOLVED FTIR SPECTRA OF B-10 POLYCYANURATE FILM DURING HEATING

### 3.3 VOLATILE DEGRADATION PRODUCTS.

Analysis of the gas phase thermal decomposition products by pyrolysis-FTIR shows no absorption bands at 1570 and 1360 cm<sup>-1</sup>, indicating that the volatile thermal degradation products contain no triazine as shown in figures 6 and 7 for the B-10 and BPC cyanate esters, respectively. In contrast, the -OCN group is present in the volatile decomposition products evolved between 435°-450°C as evidenced by the appearance of an absorption doublet at 2290 and 2250 cm<sup>-1</sup>. Also detected in the infrared spectrum are phenols, methane, ammonia, and carbon dioxide.



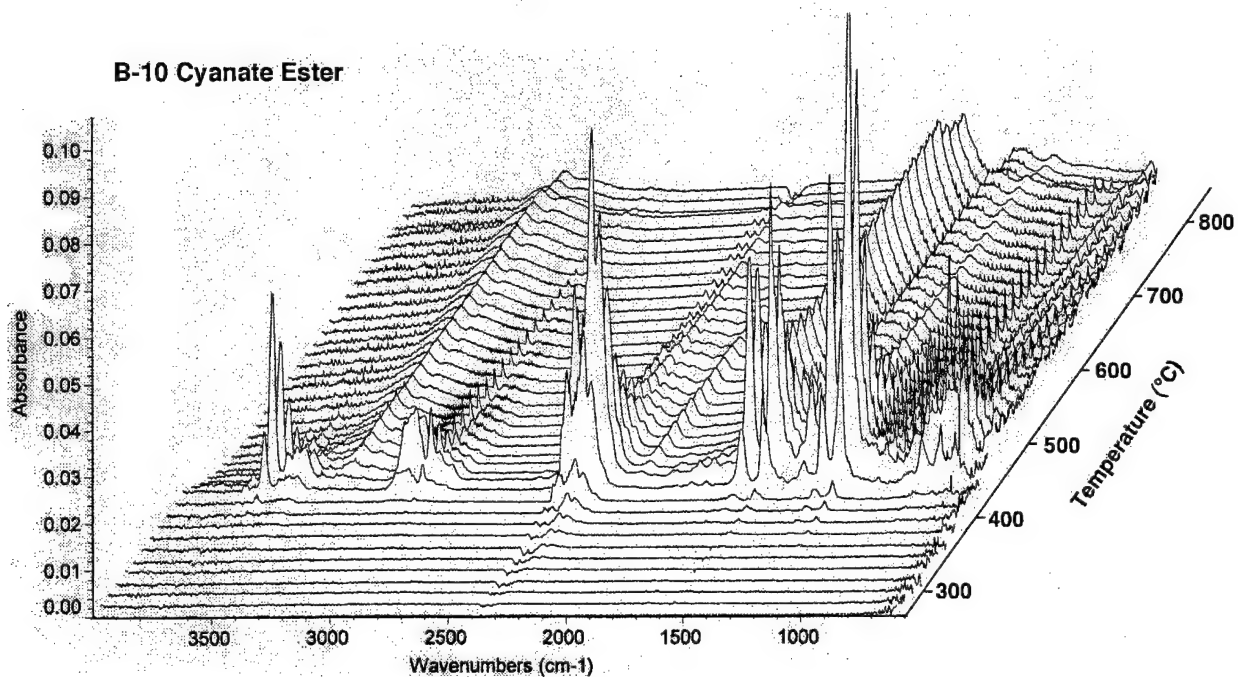


FIGURE 6. TEMPERATURE RESOLVED GAS PHASE FTIR SPECTRA OF B-10 POLYCYANURATE VOLATILE DECOMPOSITION PRODUCTS

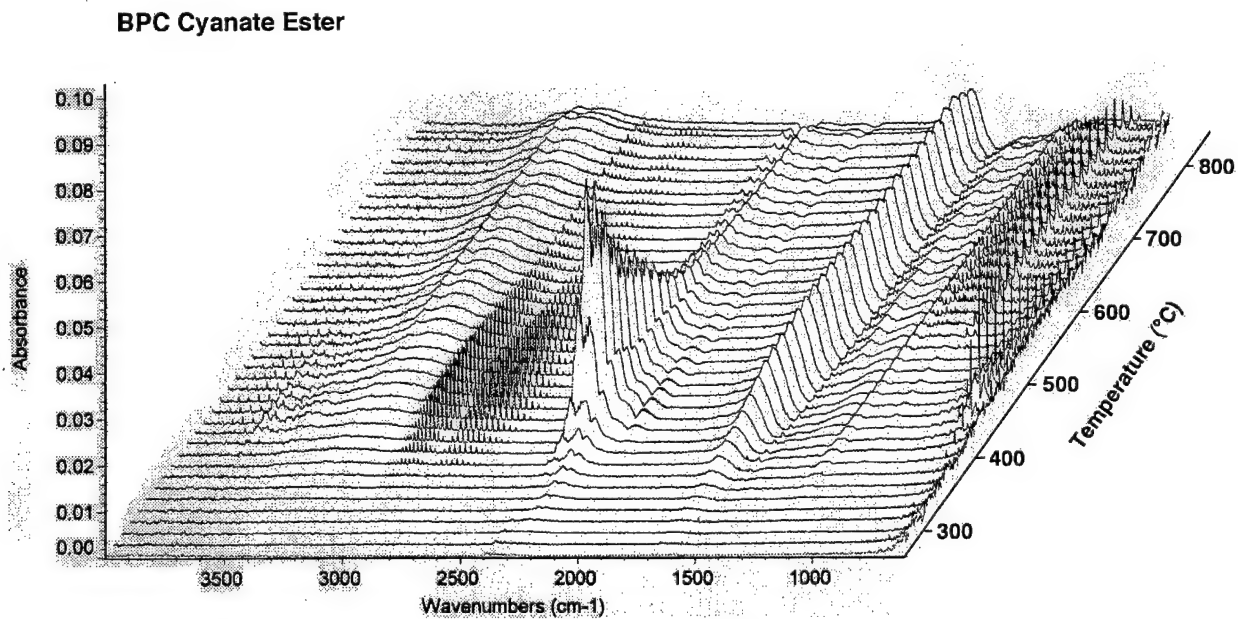


FIGURE 7. TEMPERATURE RESOLVED GAS PHASE FTIR SPECTRA OF BPC POLYCYANURATE VOLATILE DECOMPOSITION PRODUCTS

Table 3 lists the wavenumbers of the infrared absorbance doublets for the volatile decomposition products of each of the polycyanurates. All are within the  $2200\text{--}2300\text{ cm}^{-1}$  range and are separated by  $38\text{ cm}^{-1}$ .



TABLE 3. WAVENUMBERS OF THE -OCN GROUP ABSORBANCE DOUBLET FOR THE VOLATILE DECOMPOSITION PRODUCTS

Polycyanurate	$\nu_1$ ( $\text{cm}^{-1}$ )	$\nu_2$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )
XU-366	2282	2251	31
XU-71787	2283	2245	38
B-10	2282	2252	30
M-10	2290	2260	40
L-10	2287	2250	37
F-10	2283	2251	32
BPCCE	2286	2245	41
XU-371	2289	2251	38
PT-30	2288	2257	31

The gas phase bands are shifted slightly in frequency from those of the solid film of figure 5. The presence of an ether oxygen stretching band at  $1264\text{ cm}^{-1}$  in some of the gas phase spectra indicates that the -OCN group is connected to a carbon atom. The presence of  $\text{CO}_2$  is indicated by the absorption peaks at  $2360$  and  $1339\text{ cm}^{-1}$ . When the PT-30 pyrolysis gas spectrum is corrected for  $\text{CO}_2$  absorption by spectral subtraction, the doublet centered around  $2270\text{ cm}^{-1}$  persists, indicating that its origin is probably the -OCN group. Also manifest in the gas phase decomposition product spectrum is the multiplet around  $3520\text{ cm}^{-1}$  which is most likely due to amines, isoureas, or melamine derivatives [23]; the C-N band that appears at  $1172\text{ cm}^{-1}$ ; and the aromatic and substituted benzene bands at  $1513\text{ cm}^{-1}$  and in the  $900\text{-}600\text{ cm}^{-1}$  range, respectively. Aromatic amines, isoureas, and melamine derivatives can result from carbamate decomposition [23]. Further evidence of this reaction is the presence of characteristic absorption bands for phenolics near  $3740$  and  $3654\text{ cm}^{-1}$ , since phenolics can be generated by aryl carbamates [27].

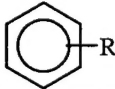
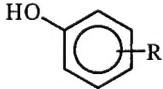
Literature reports of the thermal decomposition of cyanuric acid suggest quantitative generation of hydrocyanic acid [27 and 28]. With this in mind, it is logical that the polycyanurates, which are the esters of cyanuric acid, would exhibit similar thermal degradation reactions to yield the cyanate ester group but at higher temperature due to the increased thermal stability imparted by the phenyl ring. In addition to the lack of triazine bands in the gas phase spectra, the scanning experiments indicate that the generation of the aryl cyanates and other products by the solid during heating is rather continuous throughout the temperature range until the production of alkenic structures absorbing at  $965$  and  $930\text{ cm}^{-1}$  due to secondary decomposition processes in the char above  $600^\circ\text{C}$ . It is possible that earlier investigators missed detecting the aryl cyanate degradation fraction because gas transport temperatures were too low to maintain volatility of these species.

All of the polycyanurates contain aromatic rings in the backbone and produce similar decomposition products during pyrolysis. Table 4 shows the major decomposition products detected and identified in the pyrolysis-gas chromatography/mass spectrometry experiments. In columns 3 and 4 of table 4, R denotes alkyl substituents (methyl, dimethyl, ethyl, ethylmethyl, etc.). In column 5, labeled "Other Products," R denotes an alkyl-substituted benzyl or phenyl. PAH is polyaromatic hydrocarbons (naphthalene, azulene, indacene, etc.). Percentages assigned

to miscellaneous refer to those compounds not identified with good qualification number (uncertainty > 50%).

Substituted benzene and phenols are common to all of polycyanurate pyrolysis products, the particular substituent depending on the group linking the aromatic rings. For example, B-10 generated methylated benzenes and phenol during its decomposition. A peak in the gas chromatogram at  $m/z = 44$  is common in different abundances to all of the cyanate esters studied. The mass spectral search library identified  $\text{CO}_2$  as the closest match for this product with a very low qualification percentage based on comparison with the  $\text{CO}_2$  mass spectra and the fragmentation pattern of the molecule. The presence of peaks with  $m/z = 42, 43$ , and  $44$ , with  $m/z = 43$  the most abundant fragment, may indicate the presence of HOCN rather than  $\text{CO}_2$ . This pattern is expected for compounds containing the  $-\text{OCN}$  group [29]. The first peak in the gas chromatogram thus appears to be a mixture of HOCN and  $\text{CO}_2$ , the latter from the degradation of HOCN to amines and  $\text{CO}_2$  as suggested earlier. There is no evidence in the py-GC/MS data for the presence of ammonia or methane in the mass spectra of the volatile decomposition products because fragments with  $m/z$  less than 40 are not detected by the mass spectrometer. However, these compounds were detected in the infrared spectra of the pyrolysis gases.

TABLE 4. PERCENTAGES OF VOLATILE DECOMPOSITION PRODUCTS IDENTIFIED BY MASS SPECTROSCOPY FOR SIX POLYCYANURATES

Polycyanurate	$\text{CO}_2$ / HOCN			Other Products
XU-366	15.28	36.07	21.95	ROCN=3.6 RCN=2.6 RNH=2.5 Misc. =18.0
M-10	14.33	14.3	55.46	ROCN=2.39 RCN=1.63 RNH=3.5 Misc. = 7.67
L-10	18.04	14.79	17.82	PAH = 44.71 ROCN= 1.08 RCN= 3.57
B-10	21.2	10.1	29.13	BPA=16.1 RCN=3.92 Furanes=5.11 ROCN=2.54 RNH=3.00 Misc. =10.08
XU-371	38.52	8.7	39.8	Misc. =10.46
BPCCE	84.07	8.07	0.0	ROCN= 1.66 RCN=3.55 Misc. = 5.4

#### 4. CONCLUSIONS.

The thermal degradation chemistry of nine polycyanurates was examined. Thermogravimetry and infrared spectroscopy were used to study the mass loss process and in situ degradation chemistry, respectively, of solid samples heated at a constant rate of 10-20°C/minute. The evolved pyrolysis gases were analyzed by FTIR and GC/MS to characterize the amount and type of thermal degradation products. All of the polycyanurates exhibited the same general three-step thermal decomposition during heating at a constant rate. The consecutive process are (1) random scission and cross-linking of the hydrocarbon backbone between 400°-450°C without significant mass loss; (2) breakdown of the triazine ring between 450°-500°C with the liberation of low molecular weight volatile compounds and the formation of a primary solid residue; and (3) decomposition of the primary residue between 500°-750°C with the elimination of alkenes and hydrogen leaving a secondary, carbonaceous char containing residual oxygen and nitrogen. The amount of char is proportional to the glass transition temperature and/or carbon bond unsaturation of the monomer.

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